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Testing the steady state assumption for the Earth's surface denudation using Li isotopes in the Amazon basin

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Abstract

In this contribution we test the steady-state assumption for the surface denudation in the rivers from the Amazon basin by calculating "predicted" sediment concentration for each river using the Li isotope composition of dissolved and solid river materials. This calculation relies on a good estimation of the Li isotope composition of the bedrock drained by each River. By using the mean Li isotope composition of the major rock types from the literature, in combination with suspended sediment depth-profile and Nd isotope composition, it is possible to obtain an accurate estimation of the Li isotope composition of the bedrock. Calculated "Predicted" sediment concentration by the steady-state model agree well within a factor of two with the suspended sediment concentration derived from both decadal sediment gauging measurements and cosmogenic nuclides implying that the steady-state assumption is valid for the Amazon Rivers studied here. This has important implications for estimating the long-term erosion rates and constraining the geomorphic dynamic of watersheds using "non-traditional" isotopes.

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Keywords: Lithium isotope ; Steady-state ; Large rivers ; Shales ; Erosion rate

1. Introduction

Large rivers collect and transport the dissolved and solid products of the denudation of the continental crust, derived from chemical weathering and erosion processes, respectively. Compared to the bedrock, soluble elements are usually enriched in the dissolved load of rivers, and depleted in river sediments. The complementarity between dissolved and suspended sediment loads can be used with a mass-balance approach to test whether denudation in a large river basin operates at steady state or not[1]. In particular, a denudation at steady state indicates that in the river basin, the rate of soil formation is equal to the rate of soil removal by physical erosion + silicate weathering, or in other words that soils have a constant depth over the timescale corresponding to the residence time of denudation

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products in the weathering zone. If verified, the steady state assumption is very useful for (i) simplifying mass balance budgets[1–3], (ii) predicting the long-term chemical or physical erosion fluxes in watersheds[1,4], (iii) determining the chemical composition of the drainage basin bedrock[1] or (iv) characterizing the transient evolution of landscapes (e.g. are soils currently thickening, being eroded or in equilibrium?)[4]. Until now, steady state conditions have been tested in large rivers using major and trace elements composition[1], uranium-thorium radioactive series[4] and recently "non-traditional" isotope systems[2,3]. In this contribution, we test the steady state assumption and explore the related limitations and uncertainties of the approach in the Amazon River basin using lithium (Li) isotopes. Li isotopes are particularly powerful for such approach because they are strongly fractionated between water and secondary minerals during weathering and are not influenced by the organic cycle. At steady-state the Li isotope composition (δ^7Li) of the various compartment (rock, water and sediments) are linked to the Li fluxes by the following equation[2]:

$$\frac{\delta^7 Li_{diss} - \delta^7 Li_{rock}}{\delta^7 Li_{sed} - \delta^7 Li_{rock}} = -\frac{1 - w^X}{w^X}$$

where δ^7Li_{rock}, δ^7Li_{diss}, δ^7Li_{sed} are respectively the Li isotope composition of the bedrock, dissolved load and sediments and "w^{Li}" is the fraction of Li transported in the dissolved load compared to the total riverine Li (solid + dissolved). This equation can be re-arranged to enable calculation of "predicted" sediment concentration of the river ([Sed], in g/L) using the Li isotope composition and Li content in water (in ppb) and sediments (in ppm):

$$[Sed] = -\frac{[Li]_{diss}}{[Li]_{sed}} \times \frac{\delta^7 Li_{diss} - \delta^7 Li_{rock}}{\delta^7 Li_{sed} - \delta^7 Li_{rock}}$$

These predicted sediment concentrations can then be converted into erosion rates after multiplication by river discharge, and then can be compared to actual measurements of erosion rates or sediment concentration to test the steady state assumption.

An accurate determination of the sediment concentration using Eq. (2) relies on the good knowledge of the lithium isotope composition of the bedrock (δ^7Li_{rock}) and of the Li concentration and Li isotope composition of the water (δ^7Li_{diss}) and sediments (δ^7Li_{sed}). First, for $[Li]_{sed}$ and δ^7Li_{sed} it is important to take into account the variability of suspended sediments δ^7Li with depth[5]. In the following, we use depth-integrated sediment concentration and isotope composition when known, otherwise we rely on surface sediment characteristics (Table 1). Secondly, it is important to have representative values of $[Li]_{diss}$, especially with respect to seasonal variability. Here we use the mean dissolved Li concentration and isotope composition of all the samples available for each sampling location[6]. Most of the rivers have been sampled twice, during high and low water stage and show limited temporal variability in δ^7Li_{diss} (less than 2‰), except the Madeira and Negro rivers which show a more pronounced seasonality. In the following, we show how the last parameter, δ^7Li_{rock}, can be determined accurately, and thus demonstrate why Li isotopes are particularly well suited for testing steady state mass balances.

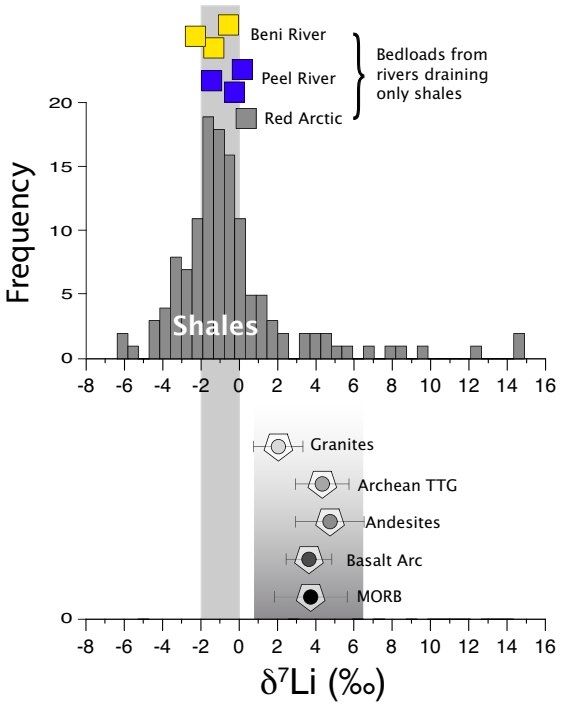

Fig. 1. (a) Mean Li isotope composition of the major rock types. (Top) Histogram representing the Li isotope composition (δ^7Li) of shale samples from the literature (n = 151; compiled in ref [5,7]); the yellow, blue and grey squares corresponds to the δ^7Li_{sed} of river sands from rivers draining only shale rocks[5]. (Bottom) Mean δ^7Li of granites, Archean TTG, andesites, basalts arc and MORB[8,9] from the literature (error bars represent 1 standard deviation). (b) Modeling of the bedrock Li isotope composition as a function of the proportion of shales for a mixed andesite-shale basin (blue curve, valid for *e.g.* Solimões, Pastaza or Ucayali rivers) and a mixed granitic-shale basin (red curve, valid for *e.g.* Negro, Tapajos, Trombetas and Urucara rivers). (c) Modeling of the uncertainty on the estimation of δ^7Li_{rock} using linear error propagation.

2. Estimation of the Li isotope composition of the bedrock (δ^7Li_{rock})

In large river basins, the estimation of the mean composition of the bedrock is potentially a significant source of uncertainty because of the mixed lithology. This is especially true for rivers having a low proportion of dissolved Li (low w^{Li})[2] as the term "$\delta^7Li_{sed} - \delta^7Li_{rock}$" in eq. (2) is close to 0 because in this case the sediments are rich in primary minerals[9]. In the following, we use of the mean composition of major rock sources to estimate the composition of the bedrock at the scale of large tributaries of the Amazon. This is justified because large river basins drain vast portion of the continental crust and are less sensitive to small-scale rock heterogeneities (*e.g.* high δ^7Li_{rock} of the rocks in a Greenland watershed[10]). Two main features makes the estimation of δ^7Li_{rock} easier than for other chemical or isotope proxies: (i) the range of mean δ^7Li of the major rock types is relatively narrow (Fig. 1) compared to the fractionation between dissolved and solid load (which is as high as 30-40‰)[6], (ii) shales, that are very abundant in the upper crust, have much higher Li concentrations (70-80 ppm) compared to granitic rocks (22 ppm), andesites (12 ppm) and basalts and are buffering the continental crust submitted to weathering and erosion for Li. Therefore, the

Li isotope composition of the bedrock of large river basins will be close to the mean composition of the shales even in presence of other rock types. It is therefore possible to calculate the mean δ^7Li_{rock} as a function of the proportion of shales in the basin (Fig. 1). The largest uncertainty on δ^7Li_{rock} are in fact obtained for river basins having bedrock dominated by volcanic rocks (such as andesite) with a small proportion of shales (5 to 40%, Fig. 1). Despite the large range of δ^7Li in shales, the great majority of the samples and the river sands from monolithological shale watershed (that are "integrative" samples) have a δ^7Li comprise between 0 and -2‰. We therefore use here a mean δ^7Li_{rock} of -1±1‰ for shales.

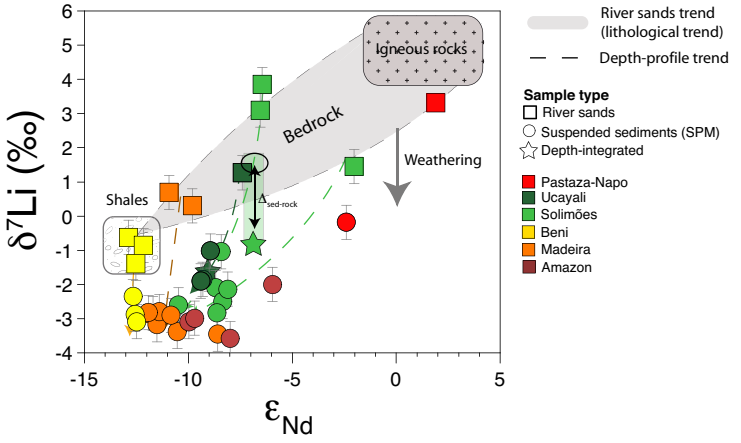

Fig. 2. Li isotope composition of river sediment (δ^7Li) as a function of their Nd isotope composition (ε_{Nd}). Shales and andesites end members are estimated from the litterature[5,11]. Each river depth-profile defines a trend with lower Li isotope value in the suspended sediments than in coarse river sands collected at the channel bottom because suspended sediments are more affected by weathering. The great majority of suspended sediments are derived from erosion and weathering of shales. Depth-integrated δ^7Li_{sed} values are represented by a star (here only for the Solimões and Ucayali rivers, for clarity). For the Solimões River, two depth-profile trends are drawn to take into account the variability in Nd isotope composition of river sands (due to the variable ε_{Nd} values of Andean Igneous rocks[11]).

For rivers having high w^{Li} and draining the Amazonian shield (Negro, Tapajos, Trombetas and Urucara rivers), the bedrock is dominated by Precambrian shield rocks which composition is similar to granites with a small proportion (< 30%) of sedimentary rock cover[1]. Therefore, using Fig. (1b-c) δ^7Li_{rock} is estimated to be +1.0 ± 1.7‰. In these rivers, δ^7Li_{sed} is significantly lower than δ^7Li_{rock}, so the uncertainty on δ^7Li_{rock} will not affect the accuracy the calculation of erosion rates using eq. (2).

For the rivers having low w^{Li}, the large uncertainty on δ^7Li_{rock} is critical. This is particularly important for the Solimões, Ucayali and Pastaza rivers, for which using the mixing diagram Fig. 1b-c is problematic as their bedrock contain less than 70% of shale-derived sediments[5]. A more accurate value of $\delta^7Li_{sed} - \delta^7Li_{rock}$ can be estimated based on the Nd isotope composition (ε_{Nd}) of their sediments and sands (Table 2). Conversely to Li isotopes, ε_{Nd} is not sensitive to weathering processes and river Nd reflects the composition of the source rocks from which it is derived. As river sands are composed predominantly by unweathered bedrock fragments[5], the variability of δ^7Li and ε_{Nd} of sands reflect a lithological trend corresponding in the Andes to a mixture between shales and igneous rocks such as andesites (Fig. 2). Suspended sediments plot below the trend defined by river sands because they contain secondary minerals formed during the present-day weathering cycle that have δ^7Li values lower than δ^7Li_{rock}. In Fig. 2, weathering leads to a decrease of δ^7Li with no change of the ε_{Nd}. The $\delta^7Li_{sed} - \delta^7Li_{rock}$ value for each river can be obtained by projecting vertically (same ε_{Nd}) the depth-integrated δ^7Li_{sed} value (calculated using a method described elsewhere[12]) on the trend defined by river sands (black arrow in Fig. 2 for the Solimões River). The estimated $\delta^7Li_{sed} - \delta^7Li_{rock}$ values using ε_{Nd} are reported in Table (1) and have a lower uncertainty than those obtained using the method of Fig (1).

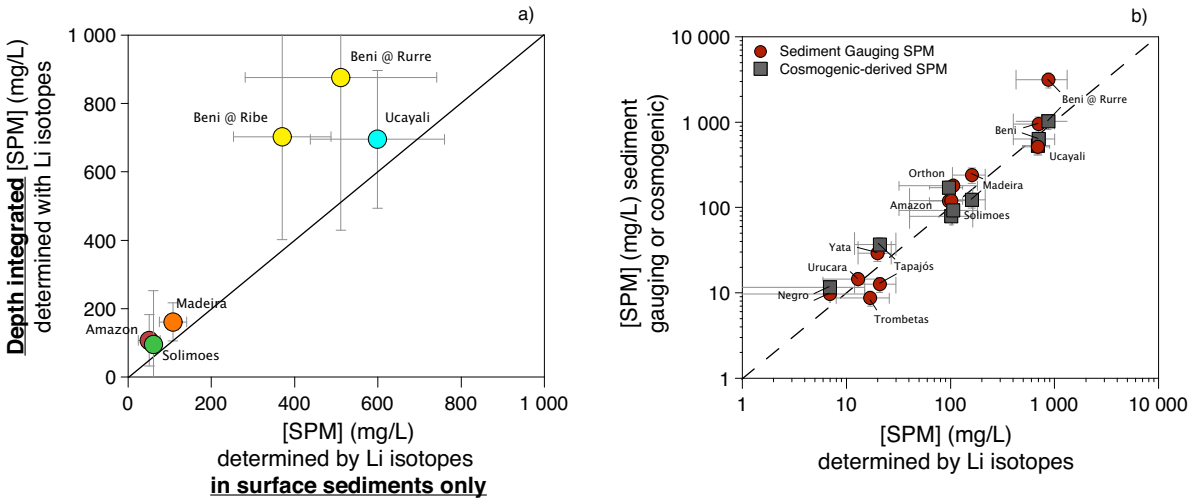

Fig. 3. (a) Comparison between steady state sediment concentrations (eq. (2)) determined using the depth-integrated δ^7Li_{sed} and Li concentration values and surface sediments δ^7Li_{sed} and Li concentration. (b) Comparison between the steady state sediment concentration using Li isotope and the measured sediment concentration based on sediment gauging and cosmogenic nuclides[13]. The dashed line is the 1:1 line.

3. Calculation of sediment concentration using the steady state equation and comparison with measured sediment concentrations

With accurate estimates of the bedrock Li isotope composition in each river basin, we can now calculate a "predicted" sediment concentration using eq. (2). The calculated sediment concentration from the steady state model can be compared to both suspended particulate matter concentrations (SPM) derived from decadal sediment gauging or from cosmogenic nuclide concentrations in river sands[13]. It should be emphasized that cosmogenic nuclides-derived denudation rates integrate erosion rates over a longer time period than sediment gauging[3]. At first order, calculated and measured suspended sediment concentration are in good agreement for all the rivers (Fig. 3). This implies that from the Li isotope point of view, the erosion-weathering system operates at steady state in the Andes and the lowlands in the Amazon basin, conversely to what was found by others studies[1,4,12]. Two explanations can be offered at this stage:

(1) Unlike in previous studies based on U-series[4], here we take into account the variability of the sediment chemical and isotopic composition with depth in the channel. The same calculation using only surface sediments for the Beni, Madeira and Solimões rivers results in lower predicted sediment concentrations (Fig. 3a), closer but still slightly higher than the values calculated with U-series[4]. We note however that the predicted sediment concentration from the lowland rivers (Orthon, Yata, Negro, Tapajos, Trombetas, Urucara) agree well with the measured sediment concentration (from both sediment gauging or cosmogenic nuclides) despite not being depth-integrated. One possible reason is that these rivers (at least the Negro and Tapajos rivers) show no variation of the SPM concentration with depth[14], because their SPM contain little coarse grains and is thus less prone to hydrodynamic sorting than in others rivers.

(2) Li isotopes allow for a more accurate estimation of the composition of source rocks, compared to major elements.

4. Conclusions and perspectives

We use the lithium isotope system to test whether denudation operates at steady state in the Amazon River basin. For lithologically mixed river basins, the main source of uncertainty for this test is the Li isotope composition of the bedrock. This limitation can be circumvented by using the mean δ^7Li composition of major rocks types and the Nd

isotope composition of both river bed sands (coarse sediments) and suspended sediments (fine sediments). Predicted sediment concentration using Li isotopes in rock, water and sediments are similar within a factor of 2 to sediment gauging-derived and cosmogenic nuclide-derived sediment concentration. This implies that the steady-state assumption is valid within uncertainties for the Amazon River basins studied here.

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Appendix

Table 1: Li isotope composition and Li concentration in the bedrock, water and sediments. Predicted and measured sediment concentrations. "n" corresponds to the number of sample for each parameter.

		Bedrock	Sediment depth-profiles			Surface sediments			Dissolved load			Surface	Depth-integrated	Sediment gauging		Cosmogenic nuclides	
Rivers	Location	δ^7Li_{rock}	Li_{Sed}	δ^7Li_{Sed}	n sampling missions	$Li_{surface\ Sed}$	n	$\delta^7Li_{surface\ Sed}$	n	δ^7Li_{diss}	Li_{diss}	n	Steady-state SPM	Steady-state SPM	SPM	w^{Li}	SPM	w^{Li}
		‰	ppm	‰		ppm		‰		‰	ppb		mg/L	mg/L	mg/L		mg/L	
Beni	Rurrenabaque	-1.0 ± 0.3	71 ± 7	-1.5 ± 0.5	1	87 ± 9	1	-3.1 ± 0.5	1	10.5 ± 2.3	8.89 ± 2.70	2	562 ± 230	959 ± 447	3234	0.04	1050	0.11
Beni	Riberalta	-1.0 ± 0.3	67 ± 7	-1.3 ± 0.5	1	86 ± 9	2	-2.9 ± 0.5	2	15.7 ± 0.2	3.90 ± 0.60	2	394 ± 117	748 ± 301	980	0.06	653	0.08
Madeira	Foz Madeira	-0.8 ± 0.5	83 ± 8	-2.0 ± 0.5	2	95 ± 10	2	-3.1 ± 0.5	2	22.1 ± 3.3	1.21 ± 0.20	3	124 ± 33	167 ± 56	248	0.06	127	0.10
Amazon	Mouth	-0.5 ± 1.5	56 ± 5	-2.4 ± 0.5	2	81 ± 8	1	-3.6 ± 0.5	1	17.9 ± 1.6	0.92 ± 0.12	2	67 ± 26	125 ± 75	186	0.08	95	0.15
Ucayali	Jenaro Herrera	0.0 ± 0.2	55 ± 8	-1.8 ± 0.5	1	58 ± 6	1	-1.9 ± 0.5	1	16.7 ± 1.0	4.58 ± 0.46	1	694 ± 161	773 ± 202	527	0.14	545	0.13
Solimoes	Manacapuru	0.8 ± 0.5	39 ± 6	-2.2 ± 1.2	2	59 ± 6	3	-2.6 ± 0.5	1	14.5 ± 1.0	0.97 ± 0.14	2	61 ± 13	103 ± 62	124	0.17	81	0.24
Pastaza	Mouth	2.0 ± 1.3				26 ± 3	1	-0.2 ± 0.5	1	25.3 ± 1.0	0.97 ± 0.10	1	399 ± 269					
Orthon	Mouth	-1.0 ± 1.0				59 ± 6	1	-5.7 ± 0.5	1	11.5 ± 1.0	2.15 ± 0.22	1	97 ± 34		123	0.23	176	0.17
Yata	Mouth	-1.0 ± 1.0				100 ± 10	1	-5.3 ± 0.5	1	14.4 ± 1.0	0.56 ± 0.06	1	20 ± 7		30	0.16		
Tapajós	Mouth	1.0 ± 1.7				26 ± 3	2	-5.7 ± 0.5	2	15.3 ± 0.6	0.26 ± 0.03	2	22 ± 9		13	0.44	38	0.21
Trombetas	Mouth	1.0 ± 1.7				20 ± 2	1	-5.1 ± 0.5	1	9.0 ± 0.6	0.26 ± 0.01	2	17 ± 9		9	0.60		
Urucara	Mouth	1.0 ± 1.7				43 ± 4	1	-4.0 ± 0.5	1	11.9 ± 1.0	0.34 ± 0.03	1	17 ± 7		15	0.34		
Negro	Paricatuba	1.0 ± 1.0				44 ± 4	1	-2.7 ± 0.5	1	5.9 ± 4.0	0.23 ± 0.03	4	7 ± 8		10	0.34	12	0.30

Table 2: Li and Nd isotope composition of Amazon river sediments. Part of the Nd isotope data are from Bouchez et al.[32]

Sample name	Date	River	Location	Type	ε_{Nd}	δ^7Li
AM06_02	15/03/06	Solimoes	Manacapuru	Bedload	-6.54	3.10
AM06_03	15/03/06	Solimoes	Manacapuru	Bedload	-6.45	3.85
AM06_05	15/03/06	Solimoes	Manacapuru	Bedload	-2.02	1.45
AM06_07	16/03/06	Solimoes	Manacapuru	SPM	-8.42	-1.04
AM06_10	16/03/06	Solimoes	Manacapuru	SPM	-8.67	-2.09
AM06_11	16/03/06	Solimoes	Manacapuru	SPM	-8.34	-2.50
AM06_13	16/03/06	Solimoes	Manacapuru	SPM	-8.63	-2.83
AM06_14	16/03/06	Solimoes	Manacapuru	SPM	-10.48	-2.60
AM06_15	16/03/06	Solimoes	Manacapuru	SPM	-8.11	-2.14
AM05_18	06/06/05	Madeira	Foz Madeira	SPM	-8.59	-3.45
AM05_19	06/06/05	Madeira	Foz Madeira	SPM	-10.55	-3.38
AM05_20	06/06/05	Madeira	Foz Madeira	Bedload	-9.83	0.30
AM05_24	06/06/05	Madeira	Foz Madeira	SPM	-11.66	-2.85
AM06_34	19/03/06	Madeira	Foz Madeira	SPM	-11.55	-3.18
AM06_36	19/03/06	Madeira	Foz Madeira	SPM	-11.40	-2.79
AM06_39	19/03/06	Madeira	Foz Madeira	SPM	-11.92	-2.82
AM06_43	19/03/06	Madeira	Foz Madeira	SPM	-10.83	-2.90
AM06_44	19/03/06	Madeira	Foz Madeira	Bedload	-10.92	0.69
AM06_63	23/03/06	Amazonas	Obidos	SPM	-9.97	-3.09
AM06_64	23/03/06	Amazonas	Obidos	SPM	-9.69	-2.99
AM06_65	23/03/06	Amazonas	Obidos	SPM	-7.98	-3.58
AM01-14	02/18/01	Beni	Rurrenabaque	Bedload	-12.45	-1.39
AM07_04	05/05/07	Beni	Rurrenabaque	SPM	-12.49	-3.09
AM07_05	05/05/07	Beni	Rurrenabaque	Bedload	-12.16	-0.86
AM07_06	07/05/07	Beni	Riberalta	SPM	-12.67	-2.35
AM07_09	07/05/07	Beni	Riberalta	SPM	-12.56	-2.88
AM07_10	07/05/07	Beni	Riberalta	Bedload	-12.88	-0.62
AM08_10	25/04/08	Ucayali	Jenaro Herrera	SPM	-9.34	-1.85
AM08_13	25/04/08	Ucayali	Jenaro Herrera	SPM	-9.37	-1.90
AM08_14	26/04/08	Ucayali	Jenaro Herrera	Bedload	-7.45	1.27
AM08_17	26/04/08	Ucayali	Jenaro Herrera	SPM	-8.93	-1.02
AM08_36	04/05/08	Pastaza	Embouchure	SPM	-2.45	-0.18
AM08_37	04/05/08	Pastaza	Embouchure	Bedload	1.88	3.31

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